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ISOTOPE SEPARATION OF LASER EXCITED MOLECULES
BY USE OF SURFACE INTERACTION

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The fundamental problem with many laser excitation isotope separations now being proposed is that in order to avoid collisional energy transfer before separation they must be operated at low pressure ($\leq 10^{-3}$ torr). This seriously limits the mass transfer rate and the excitation source energy which can be absorbed for a given path length. A physical process which might be used to effect an efficient separation of vibrationally excited molecules from their less excited companions with the potential of a sizeable mass transfer rate is the surface adsorption-desorption time.

A molecule does not simply rebound from a non-reactive surface, but rather sticks to that surface for a period dependent upon the surface temperature and the energy of interaction. It then desorbs with a cosine distribution spatially at a time given by the relationship $t = t_0 \text{EXP}(\epsilon/KT)$ which can be written with appropriate approximations $t = 10^{-13} 10^{\frac{Q}{2.3 RT}}$ where Q is the heat of adsorption in kcal/mole (see Fig. 1). What with the excitation effecting the polarizability and effective size of the molecule and the very fact of additional energy exchange between adsorbed molecule and surface there can be little doubt that excitation would change the energy of interaction and, therefore, the residence time distribution. Unfortunately, too little is known about surfaces and their interaction with adsorbed molecules to make any reliable estimate of the magnitude of this effect. None the less, the effectiveness of surface interactions when used to exploit minor variations in molecules to effect separations cannot be doubted. In view of the interest in isotope separation by selective laser excitation, it would be worthwhile to experimentally explore what might be referred to for lack of a better name "Laser Illuminated Chromatography".

The following are some concepts of devices which might be used to separate laser excited molecules:

¹The Dynamic Character of Adsorption, DeBoer, J. H. Oxford 1968

Rotating Surface Adsorption Separator

This device consists of a rapidly rotating cylindrical surface (see Fig. 2) which rotates past a structure consisting of a series of plates arrayed along the radii of the cylinder. Two of these plates form a narrow aperture. The unseparated feed gas is fed into this aperture regulated to an appropriate pressure. The highly collimated and condensed beam of the excitation laser is directed along the length of the aperture just filling the aperture without touching the slit edges or surface of the cylinder. In the worst case of collisional relaxation (probability = 1.0) the distance between the excitation and the surface must be on the order of one mean free path. A clearance of .002" would mean a pressure limitation on the order of 1.0 torr for UF_6 at 250°K. The rest of the plates would be arranged at suitable angles to form "bins" each of which is pumped with a suitable high speed vacuum transfer pump. For example one might expect the first bin to be a "dump", i.e., to take care of leakage and molecules which pass the aperture in a specular fashion. The additional bins would be split at the point or angle which best separates the shifted time (now spatial) distributions of the desorption.

The obvious limitation of this method is that it requires residence time distribution shifts on the order of several microseconds to be effective at 4000 RPS (approximately the limit of current technology).

The advantages of this device are many: High quantum efficiency, aperture lengths are only limited by laser beam attenuation and collimation (and possibly engineering considerations), excitation and separator pressures of 1.0 torr or greater, continuous operation easy staging (molecules maintain chemical identity throughout).

Fig 2.

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Rotating Surface Adsorption Separator

Alternative Method for Illuminating Aperture of Rotating Surface Separator

In this method drum heating and surface damage might be serious problems.

Laser Illuminated Column Gas Chromatographic Devices

These devices would have the advantage of being able to exploit small differences in residence time to effect separation. The price one pays for this is a low quantum efficiency since one molecule must be excited and strike the surface many times to effect separation. Also, a column gas chromatograph is operated in a pulse mode and will, therefore, have a lower mass transfer than a continuous process at equivalent pressures. This may not be a very serious problem if diffusion and tailing are minimized enough to permit rapidly pulsed operation of the column.

The self-collisional relaxation conditions are identical with the rotating surface separator. (i.e., partial pressures of 1-10 torr for void dimensions on the order of 1 mil for the worst case.) The additional constraint is that the elution gas would have to be chosen for an extremely long collisional relaxation time with the molecules to be separated.

There are two basic column constructions used in chromatography, packed and capillary. Packed columns have the advantage of greater surface areas in much shorter columns and higher mass transfer rates. Unfortunately, illumination of such a column requires that the structural support (i.e., tubing) and packing be transparent to the wavelength of the excitation radiation so that the column may be illuminated transversely. Though this method is certainly possible and worth considering, the materials constraints of such a system are likely to be serious. More easily done is a column constructed of a close packed bundle of very fine capillaries. If the surface of the capillaries can be made to be highly reflective of the excitation radiation, then light entering the end of the bundle can be made to follow the column much as in fibre optics. Dividers can be put in the ends to fold the gas stream back and forth to obtain the required length of column without seriously affecting the optical conditions.

Although these methods depend upon an area of science where measurements tend to be difficult and useful separators (i.e., chromatography) are devised largely by art, the power of surface separation methods can be undoubted. It is even within the realm of possibility that surface separations of isotopes could be achieved without isotopically selective excitation but merely by the difference in interaction of excited molecules with a surface. In view of this some research effort along these lines should be done at this laboratory.

Laser Illuminated Gas Chromatographic Column

Column consisting of a great number of very fine (.001") thin wall capillaries close packed and divided at the ends to fold the gas stream back and forth.

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